On an Inversion Point for Liquid Carbon Dioxide in Regard to the Joule-Thomson Effect.

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In a paper published recently in the 'Philosophical Transactions' "On the Thermal Properties of Carbonic Acid at Low Temperatures,"* Prof. C. Frewen Jenkin and Mr. D. R. Pye give, amongst other results, those obtained from a series of measurements of the Joule-Thomson effect for liquid CO_2 at various temperatures. These results are tabulated in Table V of their paper. They are of particular interest because, within the range of temperatures to which they correspond, they find an inversion point for the Joule-Thomson effect, *i.e.*, a temperature at which the effect changes over from being a cooling (at higher temperatures) to being a heating. As they themselves say: "No experiments on the Joule-Thomson effect for liquid CO_2 appear to have been published" previously; and as they admit that it is not easy to say what effect the presence of a trace of air (which was there) may have on their results, any method of testing them should prove of value. Such a test can be made by utilising the values of the specific volumes of liquid CO_2 which they give in a diagram on p. 78 of their paper.

Method of Test.

If the drop of pressure employed may be treated as a differential the Joule-Thomson effect is given by the equation

$$C_p\left(\frac{\partial T}{\partial p}\right)_{E+pv} = T\left(\frac{\partial v}{\partial T}\right)_p - v = T^2\frac{\partial}{\partial T}\cdot\left(\frac{v}{T}\right)_p.$$

The inversion point must therefore correspond to a minimum (or maximum) value of v/T.

Application of Test.

I have read off from the diagram of specific volumes the values at various pressures and temperatures and calculated the ratios v/T. These are tabulated below :—

* 'Phil. Trans.,' 1913, A, No. 499.

p = 400 lb./sq. in.

t.	T.	v.	$\frac{v}{T} \times 10^5$.
° C.	Abs.		
−16·5	256·5	0·974	380
−27	246	0·933	379·3
−36	237	0·900	379·7

p = 500 lb./sq. in.

t.	T.	v.	$\frac{v}{T} \times 10^5$.
° C.	Abs.		
−4·6	268·4	1·042	380
−16·5	256·5	0·970	378·2
−27	246	0·929	377·6
−36	237	0·897	378·5

p = 600 lb./sq. in.

t.	T.	v.	$\frac{v}{T} \times 10^5$.
° C.	Abs.		
+5·7	278·7	1·119	401·5
−4·6	268·4	1·031	384·1
−16·5	256·5	0·967	377·1
−27	246	0·926	376·4
−36	237	0·895	377·6

All these three sets concur in giving a minimum value of v/T at a temperature not much removed from −24° C. The inversion point actually found experimentally lies between −20·7° and −31°, and by plotting their cooling effects one finds it to be at −28° C., the high pressure being between 668 and 664 lbs./sq. in., and the low pressure between 433 and 360. The mean pressure is therefore about 500 lb./sq. in. Thus, the rather remarkable result that an inversion point exists near the point found is confirmed. The result is remarkable, because it implies that liquid CO_2 is in this region behaving very nearly like a perfect gas, its volume being nearly proportional to the absolute temperature.

It may be added that 500 lb./sq. in. is about 0·46 times the critical pressure, and −28° C. is about 0·81 times the critical temperature; and that these are approximately co-ordinates of an inversion point for any van der Waals liquid.